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PATENT SPECIFICATION

NO DRAWINGS

933,791



Date of Application and filing Complete Specification: April 7, 1961.

No. 12662/61.

Application made in Germany (No. C21172 IVb/12a) on April 9, 1960.

Complete Specification Published: Aug. 14, 1963.

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Index at acceptance:—Class 2(3), C1G(4B:5B:6A2:6B5).

International Classification:—C07d.

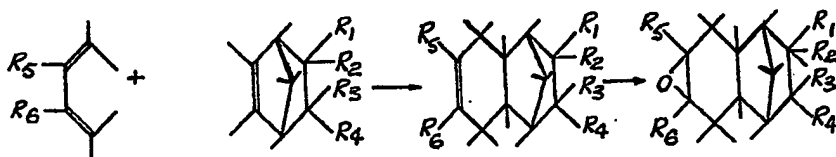
COMPLETE SPECIFICATION

Process for the manufacture of Saturated Polycyclic Halogen-Containing Epoxides

We, CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE G.M.B.H., a Company recognised by German law, of 20, Zielstattstrasse, München 25, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

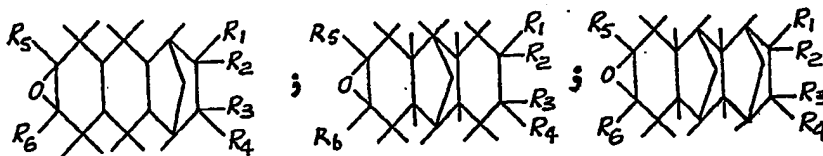
The present invention provides a process for the manufacture of saturated polycyclic halogen-containing epoxides, other than compounds having a steroid skeleton, from polycyclic olefines whose olefinic carbon atoms are not substituted by halogen and belong to a 5- or 6-membered carbocyclic ring which is fused with adjacent carbon atoms to a saturated carbocyclic ring system. The term "polycyclic olefines" as used in this connection means olefines with at least 3 condensed carbocyclic ring systems, the cyclic unit consisting of 5 or 6 carbon atoms. It has been observed that such olefines can be converted in good yields by known epoxidising methods, if desired in the presence of an inert diluent, into the corresponding, very reactive epoxides, accompanied by saturation of the olefinic bond.

In view of the varied possibilities of manufacturing polycyclic, halogen-containing olefines the epoxides of the invention can be prepared in a variety of ways. For example, bicyclic halogen-olefines are converted by the Diels-Alder condensation with an acyclic diene such, for example, as butadiene or a homologue thereof, into tricyclic halogen-olefines which are then epoxidised. The reaction proceeds, for example, according to the following scheme:

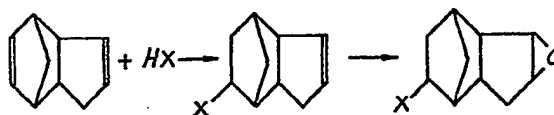


wherein R_1 to R_4 represent at least one halogen atom or a residue containing halogen, whereas R_5 and R_6 are hydrogen or residues free from halogen. The other substituents of the epoxides may be of any desired kind.

By suitably repeating this principle of the synthesis, it is possible to manufacture not only the tricyclic epoxide described above but also tetracyclic, pentacyclic and higher halogen-containing epoxides having, for example, the following constitution:



According to another way of preparing the halogen-containing polycyclic epoxides of the invention, the starting material used is a polycyclic, condensed diolefin which is converted into the corresponding polycyclic halogen-olefine in known manner by adding on 1 molecular proportion of hydrogen halide thereto. As has been observed, the latter products can likewise be converted by known methods into epoxides. The sequence of the reactions involved may be represented, for example, by the following scheme:



where X represents a halogen atom. Also in this case the unsaturated carbon atoms are free from halogen, and all other carbon atoms may be substituted in any desired manner.

The epoxidation of the olefines referred to above is accomplished most easily with per-acids, more especially with peracetic acid, and advantageously in the presence of an inert solvent, such as chloroform, toluene, ethyl acetate, acetone or the like. Instead of a pre-formed per-acid there may be used, as in known methods, hydrogen peroxide in the presence of a carboxylic acid and of an acid catalyst. Likewise suitable for manufacturing the epoxides of the invention are the known epoxidation methods using hydrogen peroxide in the presence of sodium tungstate, or organic per-compounds such as tertiary butyl hydroperoxide. The amount of per-compound to be employed advantageously ranges from 1.05 to 1.2 molecular proportions per molecular proportion of the halogen-containing olefine.

The temperature at which the epoxidation is to be performed depends on the reactivity of the ethylene bond. It has been shown that the ethylenic bond is easier to epoxidise when its distance from halogen is greater. In general, a temperature within the range of 0 to 40°C is advantageous, but it is also possible to use a temperature below or above said range. When higher temperatures are employed, the known precautionary measures, such as using a low carboxylic acid concentration and an inert diluent, must be taken. The epoxidation is continued until, when the reaction mixture is analysed, it no longer reveals a further drop in the content of peroxidic oxygen. In most cases, 80 to 90% of the double bond content undergoes epoxidation.

The epoxidation mixture is worked up in known manner by washing out the carboxylic acid and unconsumed per-acid by means of diluted sodium carbonate solution, whereupon only the solvent or the solvent and the carboxylic acid are distilled off under reduced pressure. In general, the crude epoxide is thus obtained in crystalline form or in the form of a waxy substance which solidifies on cooling.

The epoxides are purified by fractionation in vacuum or by recrystallisation, for example from a suitable petroleum fraction; the yield is between about 70 and 85%. The epoxides prepared in accordance with the invention are insoluble in water, generally sparingly soluble in aliphatic hydrocarbons and readily soluble in polar solvents such

as halogenated hydrocarbons, esters, ketones ethers, alcohols and in aromatic hydrocarbons.

The halogen-containing epoxides of the invention are polyfunctional. They are capable of reacting either by way of the epoxy group or by way of the halogen. They are suitable as components for slow-burning epoxy and polyester resins, curing agents or adhesives; as stabilisers for halogen-containing polymers; as raw materials for plasticisers and as pesticides.

The following Examples illustrate the invention:—

EXAMPLE 1

91.0 grams (0.5 mol) of 3-chloro-1:4-methano- $\Delta^{6:7}$ -octahydronaphthalene (prepared by Diels-Alder condensation of butadiene with dehydro-nor-bornyl chloride) were dissolved in 250 grams of chloroform. In the course of 1 hour, while cooling to 0 to 5°C, 123 grams (0.62 mol) of peracetic acid of 38.5% strength (whose content of free sulphuric acid had been neutralised with sodium acetate) were stirred in. The reaction mixture was then stirred at 0°C, and its content of peroxide oxygen was periodically determined. After a total reaction period of 9 hours the consumption of oxygen was substantially completed.

To neutralise the reaction mixture it was stirred into excess sodium carbonate solution cooled with ice. The neutral chloroform solution of the epoxide was separated, the aqueous phase extracted with 3 x 50 cc of chloroform, and the chloroform solutions were dried over sodium sulphate and then distilled. On evaporation of the chloroform, there remained the crude epoxide from which, by fractionation under reduced pressure, there were obtained 92 grams of 3-chloro-1:4-methano-6:7-epoxy-decahydronaphthalene.

Boiling point: 105.5—106.5°C under 0.6 mm Hg pressure.

Analysis: $C_{11}H_{15}ClO$. Molecular weight 198.70

	calculated	found
Chlorine:	17.84%	17.40%
Oxirane oxygen:	8.05%	8.02%

EXAMPLE 2

50 grams (0.25 mol) of 3-chloromethyl-1:4-methano- $\Delta^{6:7}$ -octahydronaphthalene (prepared by Diels-Alder condensation of butadiene with the adduct of allyl chloride and cyclopentadiene) were dissolved in 150 cc of chloroform and epoxidation was carried out by stirring in 115 grams (0.3 mol) of peracetic acid of 20% strength in the course of 1 hour at 5 to 10°C. Continued stirring for 3 hours completed the consumption of oxygen. The reaction mixture was neutralised, washed with water, and the organic phase was dried. Fractional distillation produced 52 grams of 3-chloromethyl-1:4-methano-6:7-epoxy-decahydronaphthalene boiling at 111 to 113°C under a pressure of 0.8 mm Hg.

Analysis: $C_{12}H_{17}ClO$. Molecular weight 212.72

Chlorine content:	calculated	16.67%
	found	16.45%

EXAMPLE 3

62 grams (0.25 mol) of 3-chloro-1:4—9:10-dimethano- $\Delta^{6:7}$ -dodecahydroanthracene (prepared by adding butadiene on to 3-chloro-1:4—5:8-dimethano- $\Delta^{6:7}$ -octahydronaphthalene) were dissolved in 180 cc of chloroform. In the course of 1 hour 115 grams (0.3 mol) of peracetic acid of 20% strength were stirred in dropwise. After 4 hours more, the consumption of oxygen was completed. Working up of the reaction mixture yielded 61 grams of 3-chloro-1:4—9:10-dimethano-6:7-epoxy-tetradeca-hydroanthracene melting at 166 to 167°C.

Analysis: $C_{16}H_{21}ClO$. Molecular weight 264.8

	calculated	found
Chlorine:	13.39%	12.95%
Oxirane oxygen:	6.05%	6.10%

EXAMPLE 4

Chloro-dihydro-nor-dicyclopentadiene was prepared by adding hydrogen chloride on to dicyclopentadiene. 80 grams (0.43 mol) of this compound were dissolved in 240 grams of chloroform and in the course of 1 hour at 0 to 1°C. 98 grams (0.51 mol) of peracetic acid of 40% strength were stirred in. After stirring for 5 hours longer at 0 to 1°C, the consumption of oxygen ceased. Working up as described in Example 1 yielded the liquid crude epoxide from which by vacuum distillation 69 grams of chloro-epoxy-tetrahydro-nor-dicyclopentadiene boiling at 134–136°C under a pressure of 11 to 12 mm Hg were obtained in a yield of 78.8%.

Analysis: $C_{10}H_{13}ClO$. Molecular weight 184.67
Chlorine content: calculated 19.20%
found 19.10%.

EXAMPLE 5

Chloro-dihydro-nor-tricyclopentadiene was prepared by adding hydrogen chloride on to tricyclopentadiene. A solution of 50 grams (0.21 mol) of this compound in 150 grams of ethyl acetate was treated at 0 to 3°C in the course of 1 hour with 50 grams (0.25 mol) of peracetic acid of 40% strength while being stirred. To complete the epoxidation, the mixture was stirred for 14 hours at 10 to 30°C. Usual working up of the reaction mixture yielded 42 grams of chloro-epoxy-tetrahydro-nor-tricyclopentadiene as a viscous liquid boiling at 182 to 185°C under a pressure of 1.5 mm Hg in a yield of 76.4%.

Analysis: $C_{15}H_{19}ClO$. Molecular weight 250.77
Chlorine content: calculated 14.14%
found 14.35%.

WHAT WE CLAIM IS:—

1. A process for the manufacture of saturated polycyclic halogen-containing epoxides other than compounds having a steroid skeleton, wherein a polycyclic halogen-containing olefine whose unsaturated carbon atoms are not substituted by halogen and belong to a 5- or 6-membered carbocyclic ring which is fused with adjacent carbon atoms to a saturated carbocyclic ring system, is epoxidised in known manner.
2. A process as claimed in claim 1, wherein the epoxidation is performed with the aid of a per-acid.
3. A process as claimed in claim 2, wherein the per-acid is peracetic acid.
4. A process as claimed in claim 1 or 2, wherein the epoxidation is performed with the aid of hydrogen peroxide in the presence of a carbocyclic acid and an acid catalyst.
5. A process as claimed in claim 1, wherein the epoxidation is performed with the aid of hydrogen peroxide in the presence of sodium tungstate.
6. A process as claimed in claim 1, wherein the epoxidation is performed with the aid of an organic peroxide or hydroperoxide compound.
7. A process as claimed in any one of claims 1 to 6, wherein the epoxidation is carried out in the presence of an inert solvent.
8. A process as claimed in claim 7, wherein the inert solvent is chloroform, toluene, ethyl acetate or acetone.
9. A process as claimed in any one of claims 2 to 8, wherein from 1.05 to 1.2 molecular proportions of the per-compound are used to 1 molecular proportion of the polycyclic halogen-containing olefine.
10. A process as claimed in any one of claims 1 to 9, wherein the epoxidation is carried out at a temperature within the range of 0 to 40°C.
11. A process as claimed in claim 1, which is conducted substantially as described in any one of the Examples herein.
12. Polycyclic halogen-containing epoxides, whenever obtained by the process claimed in any one of claims 1 to 11.

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